

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 September 2001 (27.09.2001)

PCT

(10) International Publication Number
WO 01/70647 A1

(51) International Patent Classification⁷: **C04B 38/10**,
24/26

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(21) International Application Number: **PCT/IB01/00357**

(22) International Filing Date: **14 March 2001 (14.03.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
2000/1435 22 March 2000 (22.03.2000) **ZA**

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **METHOD OF PRODUCING A HYDRAULIC BINDER FOAM**

(57) Abstract: A method of producing a hydraulic binder foam for the subsequent manufacture of a finished product, such as a foamed building board, is disclosed. An aqueous foam is prepared from water and a foaming agent comprising a hydrophilic polymer which is soluble, miscible or dispersible in water, preferably polyvinyl alcohol. The aqueous foam is mixed with a hydraulic binder in finely divided dry particle form, to produce the hydraulic binder foam. The hydraulic binder foam may then be formed into a desired shape and the hydraulic binder allowed to set to form the finished product.

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METHOD OF PRODUCING A HYDRAULIC BINDER FOAM

BACKGROUND OF THE INVENTION

This invention relates to a method of producing a hydraulic binder foam, and to a method of making a finished product from the hydraulic binder foam.

It is well known to produce a hydraulic binder foam by introducing an aqueous foam into a paste or a slurry of the hydraulic binder in water. The foam may be produced in a foam generator by passing a stream of water containing a foaming agent such as a surfactant, a protein or a hydrophilic polymer, through a venturi, in which air is injected into the passing stream, to generate a stable foam.

For example, PCT/GB 98/03556 to Windsor Technologies Limited teaches a method of making a composite product by mixing (i) a hydraulic binder; (ii) finely divided lignocellulosic fibres; and (iii) water optionally containing a polyvinyl alcohol, the water being present in an amount sufficient to form a paste; introducing a foam generated from a polyvinyl alcohol into the paste and mixing to form a foamed product; forming the foamed product into a desired shape; and allowing the hydraulic binder to set to form the composite product.

The composite product may be, for example, a building board or the like.

Another example of the manufacture of a product from a hydraulic binder foam is disclosed in United States Patent No. 4,518,652 to United States Gypsum Company.

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A further example is disclosed in United States Patent No. 6,046,255 to Gray *et al.* A foam of very small, microscopic bubbles of surfactant, each bubble containing a small quantity of water, is mixed with a water/cement mixture having a water to cement ratio of less than 0.33. The small bubbles have a ball-bearing effect on the smaller cement and sand particles, increasing plasticity or flowability thus reducing the water requirements of the mixture. The foamed cement mixture is laid to form a desired concrete structure, and the bubbles disintegrate or transform to leave voids of similar size, uniformly dispersed throughout the concrete structure.

There is, however, always a need for another method of producing a hydraulic binder foam.

SUMMARY OF THE INVENTION

According to a first aspect of the invention, there is provided a method of producing a hydraulic binder foam for the subsequent manufacture of a finished product, including the steps of:

- (a) preparing an aqueous foam from water and a foaming agent comprising a hydrophilic polymer which is soluble, miscible or dispersible in water; and
- (b) mixing the aqueous foam of step (a) with a hydraulic binder in finely divided dry particle form, to produce the hydraulic binder foam.

The foaming agent preferably comprises polyvinyl alcohol, or a combination of polyvinyl alcohol and a protein such as gelatin.

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In step (b) the aqueous foam may be added to the hydraulic binder either batchwise or continuously, preferably in a paddle-type mixer, or the hydraulic binder may be added to the aqueous foam either batchwise or continuously.

In step (b) the aqueous foam may also be mixed with a filler in finely divided dry particle or fibre form, the filler being selected from the group consisting of:

- (i) dry inorganic particles or fibres;
- (ii) dry natural organic particles or fibres; and
- (iii) dry synthetic organic particles or fibres.

In this case, the filler may be mixed with the hydraulic binder before being mixed with the aqueous foam, or the filler and the hydraulic binder may simultaneously be mixed with the aqueous foam, or the filler may be mixed with the foam before or after the hydraulic binder has been mixed with the foam.

According to a second aspect of the invention, there is provided a method of making a finished product from a hydraulic binder foam produced as described above, including the steps of:

- (c) forming the hydraulic binder foam into a desired shape; and
- (d) allowing the hydraulic binder to set to form the finished product.

DESCRIPTION OF EMBODIMENTS

The crux of the invention is that a hydraulic binder foam is prepared by mixing a pre-generated aqueous foam comprising water and a foaming agent, with dry components, viz, the hydraulic binder and optionally a filler.

The first step is thus to prepare the aqueous foam.

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The aqueous foam is prepared from water and a foaming agent comprising a hydrophilic polymer which is soluble, miscible or dispersible in water.

The hydrophilic polymer is used in an amount of from 1% to 10% inclusive by mass of the water.

Examples of suitable hydrophilic polymers are modified starches, natural carbohydrates such as gums or seaweed colloids, semi-synthetic polymers such as the cellulose ethers, hydrogels such as homo- and co- polymer derivatives of acrylic and methacrylic acid, or the polyacrylamide polyacrylate co-polymers, and dispersions such as polyvinyl acetate and styrenated acrylics.

The preferred hydrophilic polymer is polyvinyl alcohol which may be used in an amount of from 1% to 10% inclusive by mass of the water, or preferably in an amount of from 3% to 8% inclusive by mass of the water. The volume of the aqueous foam produced from a given quantity of water is strongly influenced by the viscosity of the polyvinyl alcohol used.

The preferred polyvinyl alcohols are those having a viscosity of from 10 to 75 mPa.s inclusive, determined at a 5% concentration in water at 20°C. These include the partially hydrolysed grades with a degree of hydrolysis mol % in the range of 82% to 90%, preferably about 87%, with an ester value mg/KOH/g of 140, and residual acetyl content weight percent of 10.7. Examples of suitable polyvinyl alcohols are the Mowiol grades by Clariant, particularly grade 8/88 which has a viscosity of 12 mPa.s, grade 18/88 which is the most preferred polyvinyl alcohol and which has a viscosity of 55 mPa.s, and grade 23/88 which has a viscosity of 75 mPa.s.

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The choice of foaming agent to be used will depend on the nature of the hydraulic binder and its pH. as well as the relative hardness of the water to be used.

In certain circumstances, it may be advisable to use a combination of the foaming agent, such as for example polyvinyl alcohol, with a protein compound such as gelatin.

The aqueous foam may be prepared in any suitable manner, such as for example, using a foam generator which involves passing a stream of water containing the foaming agent through a venturi, in which air is injected into the passing stream, to generate a stable foam. Alternatively, the aqueous foam may be produced by mechanical entrainment of air into the water containing the foaming agent.

The second step of the method of the invention, viz. step (b) is to mix the aqueous foam of step (a) with a hydraulic binder in finely divided dry particle form.

By "hydraulic binder" is meant an inorganic binder which in the presence of water hydrates and sets. The hydraulic binder may be selected from the group consisting of a hydraulic cement, a calcium sulphoaluminate cement, a high alumina cement, a gypsum cement, calcium sulphate hemihydrate in either the alpha or beta form, an alkali silicate, magnesium oxychloride, magnesium oxysulphate, a pozzolanic binder such as finely ground furnace slag or fly ash, silica fume, or a mixture of two or more thereof.

The hydraulic binder must be used in finely divided dry particle form. This means that 98% or more of the hydraulic binder particles must pass through a 200 mesh or finer (i.e. a 74 micron screen or finer). For example. Portland cement typically has a Blaine of 475, i.e. 475m² per kg.

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Preferably, the aqueous foam and the hydraulic binder are mixed in a proportion of from 20 parts by weight of the aqueous foam to 100 parts by weight of hydraulic binder, up to and including 120 parts by weight of the aqueous foam to 100 parts by weight of the hydraulic binder.

For example, when 25 parts by weight of an aqueous foam are mixed with 100 parts by weight of Portland cement, there results a finished product with a density of about 900 kg/m^3 . When 45 parts by weight of an aqueous foam are mixed with 100 parts by weight of Portland cement there results a finished product with a density of about 600 kg/m^3 . When 75 parts by weight of an aqueous foam are mixed with 100 parts by weight of gypsum (calcium sulphate hemi-hydrate) there results a finished product with a density of about 300 kg/m^3 . When 100 parts weight of an aqueous foam are mixed with 100 parts by weight of gypsum, there results a finished product with a density of about 170 kg/m^3 .

In addition to the hydraulic binder which must be in finely divided dry particle form, there may also be added to the aqueous foam a filler in finely divided dry particle or fibre form.

The filler may comprise dry inorganic particles or fibres such as, for example, silica, diatomaceous earth, expanded perlite, exfoliated vermiculite, refractories such as alumina or grog, ceramic fibres, mineral fibres and glass fibres.

The filler may also comprise dry natural organic particles or fibres such as paper fibres, e.g. common mixed paper waste, paper mill sludge, pulp, cellulose and the like, or agricultural fibres such as fibres from extracted wattle bark, palm fibre, kenaf, and natural organic particles such as ground cork, bark, sawdust and ground seed.

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The filler may also comprise dry synthetic organic particles or fibres such as organic particles formed from milled thermoplastic foams, e.g. PVC, polystyrene or expanded polystyrene foams, milled thermosetting foams, e.g. phenol formaldehyde resole, or polyurethane rigid or flexible foams, and organic fibres such as carbon, aramid, polyacrylonitrile, polyvinyl alcohol, polyethylene, polypropylene, polyester and acrylics.

When the filler comprises synthetic fibres, the fibres preferably have a diameter of about 20 to 40 microns inclusive and a length of from 4 to 6 mm inclusive. When the filler comprises natural fibres, the fibres preferably have a diameter of about 20 to 40 microns inclusive and a length of from 6 to 8 mm inclusive. When the filler comprises particles, the particles preferably have a maximum dimension of less than 0,5 mm, more preferably a size similar to the size of the hydraulic binder, viz, 98% passing through a 200 mesh.

The purpose of adding one or more of the fillers is as follows:

- (i) to contribute syntactic voids in the hydraulic binder foam as a function of the low bulk density of the filler. Examples of suitable fillers in this regard are exfoliated vermiculite, ground phenol formaldehyde resole resin foam, polystyrene re-grind, cork and flexible polyurethane re-grind.
- (ii) to propagate improved properties of the hydraulic binder foam. Examples of suitable fillers here are silica flour in Portland cement where the product is subsequently to be autoclaved, bubble alumina in a calcium aluminate cement to improve the refractory nature of the product, and expanded vermiculite in a high alumina cement to improve the refractory nature of the product.

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- (iii) when the filler is a fibre, then the fibres reinforce the product and may also propagate improved sound attenuation or noise reduction coefficients of the final product.
- (iv) to enhance foam stability by air bubble entrapment, in which case a suitable filler is cellulose fibre, particularly paper mill sludge or common mixed paper waste.

As indicated above, the aqueous foam and the hydraulic binder/filler may be mixed in various ways. The various possibilities are set out below.

- (1) The aqueous foam is added to the hydraulic binder optionally mixed with the filler, either batchwise or continuously.
- (2) The hydraulic binder is added to the aqueous foam either batchwise or continuously.
- (3) The hydraulic binder is mixed with the filler and the mixture is then added to the aqueous foam either batchwise or continuously.
- (4) The hydraulic binder and the filler are simultaneously added to the aqueous foam either batchwise or continuously.
- (5) The hydraulic binder is added to the aqueous foam, whereafter the filler is added to the aqueous foam (or *vice versa*) either batchwise or continuously.

Preferably, the aqueous foam is added to the hydraulic binder in a paddle-type mixer.

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It is surprising that the adding of a dry particulate material, i.e. the hydraulic binder optionally with the filler, to a pre-generated aqueous foam, produces a hydraulic binder foam with superior properties to that which can be produced by adding an aqueous foam to a slurry or a paste, i.e. a wetted product containing the hydraulic binder.

In other words, it has been found that pre-generating an aqueous foam and then adding to this directly the dry product, or alternatively, adding the dry product to the pre-generated aqueous foam with mixing, produces an excellent hydraulic binder foam, with a dry density in the range of from 170kg/m³ upwards, with very small cell sizes. The process is rapid with minimal equipment costs and is thus economically efficient, and dry to wet constituent ratios are consistently and easily controllable. It is a significant advantage that the water to hydraulic binder ratio may be reduced significantly as compared to wet-to-wet processes, more particularly at the lower finished product densities. The reason for this is that a paste does not have to be pre-formed and at pourable consistencies in order to minimise surface tension.

It is particularly surprising that this method of mixing is effective in that one would expect the addition of a dry particle to an aqueous foam, more particularly a particle not soluble in water, would result in immediate foam collapse or at least the coalescence of air cells resulting in a coarse, variable and unreliable hydraulic binder foam. As indicated above, this is not the case with the method of the invention.

Various other components may be added into the hydraulic binder foam to provide the hydraulic binder foam with specific desired properties. These additives include:

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- (i) Additives that promote resistance to high relative humidity, minimising softening back or sagging, such as the anhydrous silicones based on hydrogen polysiloxane, added in an amount of from 0.1% to 0.5% inclusive by mass of the hydraulic binder. Alternatively, an aqueous fluorochemical dispersion such as Zonyl 8740 or a fluorochemical solution in water such as Zonyl 9027, both by du Pont, may be mixed with the foamed binder, or more preferably post-applied as a surface or sub-surface water repellent at concentrations by mass of mixing water in the range 1% to 12%, more usually 2% to 6% inclusive.
- (ii) Reinforcing resins such as a dispersion of a natural or synthetic latex, polyvinyl acetate, a styrenated acrylic or the like.
- (iii) When the hydraulic binder is Portland cement, a solution of sodium silicate in order to propagate gelling. The solution may be added in an amount of from 1% to 7% by mass of the hydraulic binder.
- (iv) Where the hydraulic binder is a calcium aluminate cement, a gelation agent, for example lithium carbonate or a proportion of Portland cement.

After steps (a) and (b) of the method of the invention, in step (c), the hydraulic binder foam may be formed into a desired shape, for example by conventional techniques such as casting or pouring or otherwise dispensing into a suitable mould or on to a moving belt or the like.

In step (d) of the method of the invention, the hydraulic binder is allowed to set to form the final product.

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Thereafter, the final product may be used directly or be cured and dried and thereafter machined into suitable sizes and the like.

An example of the invention will now be given.

EXAMPLE

An aqueous foam is generated from a 5% solution of partially hydrolysed polyvinyl alcohol, e.g. Mowiol 4/88 by Clariant.

A dry mix is formed of a hydraulic binder, e.g. calcium sulphate β -hemi-hydrate with acrylonitrile fibres, e.g. Dolanit by Acordis Kelheim of Germany. These fibres are approximately 4mm in length and 6.7dtex.

900gm of the calcium sulphate β -hemi-hydrate mixed with 12gm of the acrylonitrile fibres, are added to 800gm of the pre-generated aqueous foam and the whole is mixed with high shear and with a driven propeller mixer to produce a very fine creamed foam, which is pumpable, stable for lengthy periods, and which provides a consistent end product with an open cellular structure and very fine cell size, and a dry density of 300kg/m³. This mix yields the minimum obtainable water to calcium sulphate β -hemi-hydrate ratio in the pourable stable wet foam mix for the final density required.

Thereafter, the hydraulic binder foam is formed into a desired shape, for example, a board shape, and the hydraulic binder is then allowed to set to form the finished product.

CLAIMS

1. A method of producing a hydraulic binder foam for the subsequent manufacture of a finished product including the steps of:
 - (a) preparing an aqueous foam from water and a foaming agent comprising a hydrophilic polymer which is soluble, miscible or dispersible in water; and
 - (b) mixing the aqueous foam of step (a) with a hydraulic binder in finely divided dry particle form, to produce the hydraulic binder foam.
2. A method according to claim 1 wherein the foaming agent comprises polyvinyl alcohol.
3. A method according to claim 2 wherein the polyvinyl alcohol has a viscosity of from 10 to 75 mPa.s inclusive at a 5% concentration in water at 20°C.
4. A method according to claim 2 or claim 3 wherein the foaming agent comprises polyvinyl alcohol and a protein.
5. A method according to any one of claims 2 to 4 wherein in step (a), the polyvinyl alcohol is used in an amount of from 1% to 10% inclusive by mass of the water.
6. A method according to any one of claims 1 to 5 wherein the hydraulic binder is selected from the group consisting of a hydraulic cement, a calcium sulphaaluminate cement, a high alumina cement, a gypsum cement, calcium sulphate hemihydrate in either the alpha or beta form,

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an alkali silicate, magnesium oxychloride, magnesium oxysulphate, a pozzolanic binder, silica fume, and a mixture of two or more thereof.

7. A method according to any one of claims 1 to 6 wherein in step (b) the aqueous foam is also mixed with a filler in finely divided dry particle or fibre form, the filler being selected from the group consisting of (i) dry inorganic particles or fibres; (ii) dry natural or organic particles or fibres; (iii) dry synthetic organic particles or fibres; or a mixture of two or more thereof.
8. A method according to any one of claims 1 to 7 wherein in step (b) the aqueous foam is added to the hydraulic binder either batchwise or continuously.
9. A method according to claim 8 wherein in step (b) the aqueous foam is added to the hydraulic binder in a paddle-type mixer.
10. A method according to any one of claims 1 to 7 wherein in step (b) the hydraulic binder is added to the aqueous foam either batchwise or continuously.
11. A method of making a finished product from a hydraulic binder foam including the steps of:
 - (a) preparing an aqueous foam from water and a foaming agent comprising a hydrophilic polymer which is soluble, miscible or dispersible in water;
 - (b) mixing the aqueous foam of step (a) with a hydraulic binder in finely divided dry particle form, to produce the hydraulic binder foam;
 - (c) forming the hydraulic binder foam into a desired shape; and

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- (d) allowing the hydraulic binder to set to form the finished product.
12. A method according to claim 11 wherein the foaming agent comprises polyvinyl alcohol.
 13. A method according to claim 12 wherein the polyvinyl alcohol has a viscosity of from 10 to 75 mPa.s inclusive at a 5% concentration in water at 20°C.
 14. A method according to claim 12 or claim 13 wherein the foaming agent comprises polyvinyl alcohol and a protein.
 15. A method according to any one of claims 12 to 14 wherein the polyvinyl alcohol is used in an amount of from 1% to 10% inclusive by mass of the water.
 16. A method according to any one of claims 11 to 15 wherein the hydraulic binder is selected from the group consisting of a hydraulic cement, a calcium sulphoaluminate cement, a high alumina cement, a gypsum cement, calcium sulphate hemihydrate in either the alpha or beta form, an alkali silicate, magnesium oxychloride, magnesium oxysulphate, a pozzolanic binder, silica fume, and a mixture of two or more thereof.
 17. A method according to any one of claims 11 to 16 wherein in step (b) the aqueous foam is also mixed with a filler in finely divided dry particle or fibre form, the filler being selected from the group consisting of (i) dry inorganic particles or fibres; (ii) dry natural organic particles or fibres; (iii) dry synthetic organic particles or fibres; or a mixture of two or more thereof.

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18. A method according to any one of claims 11 to 17 wherein in step (b) the aqueous foam is added to the hydraulic binder either batchwise or continuously.
19. A method according to claim 18 wherein in step (b) the aqueous foam is added to the hydraulic binder in a paddle-type mixer.
20. A method according to any one of claims 11 to 17 wherein in step (b) the hydraulic binder is added to the aqueous foam either batchwise or continuously.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B38/10 C04B24/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CHEMICAL ABSTRACTS 'Online! retrieved from STN Database accession no. 118:10827 XP002173111 abstract -& JP 04 260674 A (KANEKAFUCHI CHEMICAL INDUSTRY CO., LTD.) 16 September 1992 (1992-09-16) ---	1,2,6,7, 10-12, 16,17,20
X	DATABASE WPI Week 199344 Derwent Publications Ltd., London, GB; AN 1993-348253 XP002173112 -& JP 05 254959 A (SEKISUI CHEM. IND. CO., LTD.), 5 October 1993 (1993-10-05) abstract; claim 1 -----	1,6,7, 10,11, 16,17,20

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.*** Special categories of cited documents:*****A*** document defining the general state of the art which is not considered to be of particular relevance***E*** earlier document but published on or after the international filing date***L*** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)***O*** document referring to an oral disclosure, use, exhibition or other means***P*** document published prior to the international filing date but later than the priority date claimed***T*** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention***X*** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone***Y*** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.***&*** document member of the same patent family

Date of the actual completion of the international search

25 July 2001

Date of mailing of the international search report

28/08/2001

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